Effects of hydrogen on the structural and optical properties of MoSe₂ grown by hot filament chemical vapour deposition

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Abstract

The role of reactive environment and hydrogen specifically in growth and structure of molybdenum selenide (MoSe_2) nanomaterials is presently debated, and it is not clear whether hydrogen can promote the growth of MoSe_2 sheets and alter their electronic properties. To find efficient, convenient methods for controlling the nucleation, growth and resultant properties of MoSe_2 nanomaterials, MoSe_2 nanoflakes were synthesized on silicon substrates by hot filament chemical vapor deposition using molybdenum trioxide and selenium powders in pure hydrogen, nitrogen gases and hydrogen-nitrogen mixtures. The structures and composition of synthesized MoSe_2 nanoflakes were studied using the advanced characterization instruments including field emission scanning electron microscopy, micro-Raman spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy and energy dispersive X-ray spectrometry. The analysis of the growth process indicates that hydrogen can improve the formation of MoSe_2 nanoflakes and significantly alter their properties due to the high reduction capacity of hydrogen and the creation of more nucleation centers of MoSe_2 nanoflakes on the silicon surface. The study of photoluminescent (PL) properties reveals that the MoSe_2 nanoflakes can generate a strong PL band at about 631 nm, differently from the plain MoSe_2 nanoflakes. The major difference in the PL properties may be related to the edges of MoSe_2 nanoflakes. These results can be used to control the growth and structure of MoSe_2 -based nanomaterials and contribute to the development of advanced MoSe_2 -based optoelectronic devices.

Keywords: A1. Nanostructures; A3. Chemical vapor deposition processes; B1. Inorganic compounds; B2. Semiconducting materials

1. Introduction

Layered transition metal dichalcogenides with unique mechanical, electronic, optical and chemical properties are the candidate materials of electronic and optoelectronic devices [1,2]. Molybdenum diselenide (MoSe_2) is a member of a large family of layered transition metal dichalcogenides, which change their electronic structure from indirect to direct bandgap semiconducting depending on the number of MoSe_2 layers [3]. Due to the controllable electronic structure, this material is highly-promising for the development of electronic and optoelectronic devices such as transistors, photodetectors, electroluminescence devices, and solar cells [4-6]. This is why MoSe_2 nanomaterials have attracted significant recent attention and have been a subject of extensive studies including materials synthesis and properties [7].

Common methods of MoSe_2 nanomaterial synthesis include solution-based techniques, electron beam evaporation, and vapour deposition [8-10]. In particular, MoSe_2 nanomaterials have been extensively prepared by chemical vapour deposition (CVD) using molybdenum trioxide (MoO_3) and selenium (Se) as source materials in various gas environments [10-13]. For example, MoO_3 and Se powders or Se pellets were used as Mo and Se sources to synthesize the MoSe_2 sheets in gaseous environments of pure hydrogen or gas mixtures of hydrogen with argon [12-14]. These results suggest that hydrogen acts as a reducing atmosphere thereby playing an important role in the growth of MoSe_2 sheets. Some experiments [14] did not observe the formation of MoSe_2 sheets in the absence of hydrogen. However, it was also reported [11] that MoSe_2 sheets can effectively grow without hydrogen. The likely reason behind this is partial reduction of MoO_3 powder by Se vapor to form MoO_{3-x} species followed by further selenizing to form MoSe_2 species in the gas environment.

These examples suggest that there is a *controversy* in the current understanding of the effects of hydrogen on the growth of MoSe₂ nanomaterials. Indeed, *how does hydrogen affects the growth and structure of MoSe₂ nanomaterials? Can hydrogen alter important properties of molybdenum diselenide?* These questions motivate this study which aims to synthesize MoSe₂ nanomaterials in different gas environments, investigate their growth process, morphology and microstructure, and demonstrate the key role of hydrogen.

In this work, the MoSe₂ nanoflakes were synthesized on silicon substrates by hot filament chemical vapor deposition (HFCVD) using MoO₃ and Se powders as Mo and Se sources. The temperature of hot filaments in the HFCVD system reaches ~800 °C, thus well exceeding the substrate temperature [15]. As a result, reactive gases easily decompose at the hot filaments, and a high temperature difference is maintained between the precursor source and substrate where the decomposed precursors are deposited. This process is quite different from the common substrate-heated CVD systems where the decomposition of precursors and deposition of synthesized materials proceed in gas phase on the substrate surface. These factors increase the growth rate of deposited materials including MoSe₂ nanoflakes, that is why we have used the HFCVD system for syntheses of MoSe₂ nanoflakes. During the growth of MoSe₂ nanoflakes, pure hydrogen, nitrogen gases and hydrogen-nitrogen gas mixtures were employed. The characterization results show the formation of MoSe₂ nanoflakes with different structures, which indicates that hydrogen plays a promotive role for the growth of MoSe₂ nanomaterials. The effects of hydrogen on the growth and structure of MoSe₂ nanoflakes are studied and plausible growth model and reaction pathways are proposed. In addition, the photoluminescence (PL) properties of MoSe₂ nanoflakes are studied and the PL results exhibit the main PL band at about 631 nm and the structure-dependent PL intensity. These findings can be used to control the growth and structure of MoSe₂-based nanomaterials and are relevant to the development of next-generation MoSe₂-based optoelectronic devices.

2. Experimental and Characterization Details

The synthesis route of MoSe₂ nanomaterials is similar to the procedures described in our previous work [15]. Before the growth of MoSe₂ nanoflakes, silicon substrates were sequentially cleaned in methylbenzene, acetone and alcohol ultrasonic solutions for 15 min, respectively, and then boiled in the mixing solution of ammonia and hydrogen peroxide in deionized water for 15 min at 75 °C. The MoSe₂ nanoflakes were then grown in HFCVD system described in detail elsewhere [15]. Briefly, a heating system of three tungsten filaments heated to ~1800 °C and a silica boat for source materials were installed in the CVD chamber. The distances from the filaments to silica boat and silicon substrates were about 13 and 10 mm, respectively. When filaments are heated, the substrate surface temperature reaches ~900 °C according to the thermocouple measurements. To efficiently heat the source materials by thermal radiation of hot filaments, the silicon substrate was cut into a rectangular shape with length and width being larger and smaller than the diameter of the silica boat, respectively.

After placing the rectangle silicon wafer and silica boat with the source materials in the CVD chamber and evacuating the CVD chamber to the pressure lower than 2 Pa, the reactive gases were supplied into the chamber. Once the pressure increased to $\sim 2 \times 10^3$ Pa, the evacuation valve was adjusted to stabilize the pressure at this level. In this case, the silicon surface was heated up by the hot filaments for 6 min to ~900 °C. In this work, a series of samples were prepared under different conditions (listed in Table 1) using MoO₃ powder and Se powder.

Table 1. Growth conditions of MoSe₂ nanoflakes.

Sample	MoO ₃ (g)	Se (g)	H ₂ (sccm)	H ₂ +N ₂ (sccm)	N ₂ (sccm)
A	0.06	1.00	50	—	—
B	0.06	1.00	—	25+25	—
C	0.06	1.00	—	—	50

To confirm the repeatability of experiments, we grew the samples using high flow rate and pressure of pure hydrogen and nitrogen (these data are shown in the Supporting Information).

The morphologies of MoSe₂ nanoflakes were investigated using Hitachi S-4800 field emission scanning electron microscope (FESEM) operated at a high voltage of 15 kV, and FEI Technai G2 transmission electron microscope (TEM) operated at 200 kV. The composition of MoSe₂ nanoflakes was studied by HR 800 micro-Raman spectroscopy using a 532 nm line of semiconductor laser as the excitation source, energy dispersive X-ray (EDX) spectrometer coupled with TEM, and ESCALAB 250 X-ray photoelectron spectroscopy (XPS) using an Al K α X-ray source. The PL properties of MoSe₂ nanoflakes were studied using HR 800 micro-Raman spectroscopy with a 532 nm line of semiconductor laser as the excitation source, where the diameter of the laser spot was approximately 2 μ m.

3. Results and discussion

3.1 Structure and composition of MoSe₂ nanoflakes

Figure 1 shows FESEM images of samples A, B and C deposited in various process environments shown in Table 1. The nanomaterials are composed of diversified nanoflakes tilted with respect to the silicon substrate, but their morphologies are quite different depending on the reactive gas.

Fig. 1. FESEM images of samples A, B and C grown in H_2 , N_2+H_2 , and N_2 gases, respectively. The insets are the high resolution FESEM images of the same samples. Areas marked by dashed circles show the aggregation of nanoflakes, indicating that the nanoflakes grow in a layer-by-layer mode. The right panel shows three-dimensional reconstruction of the surface morphologies of samples A, B and C, respectively (heights are conventional, elevations were rendered proportionally to the tint at FESEM images). Difference in topology is clearly visible.

Fig. 2. Cross-sectional FESEM images of samples A and C. The parts marked by white and red rings in the images clearly show the tilt growth of nanoflakes and some newly nucleated nanoflakes on nanoflake surfaces, respectively.

Comparing Fig. 1c with Fig. 1a and 1b, one can notice from high resolution (HR) FESEM insets that the surfaces of nanoflakes in samples A and B are rough compared to that of sample C. The insets in Fig. 1 were used to assess the thickness of typically thin nanoflakes, being of about 10 nm. Moreover, the areas marked by dashed circles obviously show the aggregation of nanoflakes at one spot, which indicates that the nanoflakes grow in a layer-by-layer mode.

Fig. 3. Raman spectra of samples A-C. Every spectrum shows three main Raman peaks, the appearance of strong A_{1g} Raman mode (out of plane vibration) and weak E_{2g} Raman mode (in plane vibration) indicates the formation of $MoSe_2$.

Table 2. Positions of Raman peaks in Fig. 2.

Sample	A_{1g} (cm^{-1})	E_{2g} (cm^{-1})	RP (cm^{-1})
A	~240.7	~284.4	~338.7
B	~241.2	~286.4	~338.6
C	~239.9	~283.8	~336.8

To further confirm the uniformity of nanoflakes and clarify the role of hydrogen in nucleation and growth, the cross-sections of samples A and C were characterized by FESEM (Fig. 2). From this figure one can see that sample A has a higher density of particles (including some nanoflakes) in the interface between silicon substrate and films than sample C, i.e., the nucleation is promoted by hydrogen due to the hydrogen reaction with the substrate surface. More detailed discussion can be found in section 3.2. As a result of faster nucleation, the growth of nanoflakes becomes slow. Indeed, Fig. 2(a) shows that the film-silicon interface is mainly composed of nanoparticles, i.e., the density of nanoflakes is low. Furthermore, the areas marked by white and red rings in the cross-sectional images clearly show the tilted growth of nanoflakes, and some new nanoflakes nucleated and grow on the formed nanoflake

surfaces. Comparing the two areas marked by red rings in Fig. 2 one can see higher density of new nanoflakes in sample A, i.e. in Fig. 2(a). Besides, Fig. 2 also shows larger nanoflakes near the interface of sample C compared to sample A.

Figure 3 shows the Raman spectra of all samples A, B and C. It can be seen that every spectrum shows three main Raman peaks, and the peak positions are summarized in Table 2. The appearance of strong A_{1g} Raman mode (out of plane vibration) and weak E_{2g} Raman mode (in plane vibration) indicates the formation of $MoSe_2$ [11,13,14]. However, the A_{1g} and E_{2g} Raman modes change with the number of $MoSe_2$ layers. Specifically, the A_{1g} mode can change from 239.0 to 243.9 cm^{-1} for monolayer and thick $MoSe_2$ sheets [11,13,14]. According to the data in Table 2, our samples are composed of multilayer $MoSe_2$ nanoflakes. The generation of RP peaks located at about 338.6-338.8 cm^{-1} is not clear, it may be related to MoO_2 since the Raman peak of MoO_2 nanostructures is located at about 339.5 cm^{-1} [16]. In other words, the samples contain oxygen impurity.

From Fig.1, the thickness of $MoSe$ nanoflakes is about ~10 nm, which means that the nanoflakes are multilayer structure [13]. In Refs. (13) and (14), the A_{1g} peaks of monolayer $MoSe_2$ sheet are reported at about 239 and 241.2 cm^{-1} , respectively. The A_{1g} peaks of our samples approach to these reported values, but the FESEM results indicate that the $MoSe_2$ nanoflakes are composed of multilayer $MoSe_2$ sheets, and hence, the A_{1g} peak of our samples should be located at about 243-244 cm^{-1} intrinsic to thick $MoSe_2$ sheets [11, 14]. The shift of A_{1g} peaks of our samples compared to the reported values indicates the oxygen incorporation in the $MoSe_2$ nanoflakes, which is evidenced by the blue shift of A_{1g} peak of MoS_2 sheets caused by the doping of oxygen [17].

Fig. 4. TEM micrographs (a-c) and SAED patterns (d-f) of samples A, B and C. The selected area electron diffraction patterns shown in the right panel indicate that the MoSe₂ nanoflakes have a crystalline structure.

To confirm the fine structure and composition of MoSe₂ nanoflakes, all samples were separated from silicon substrates and studied by TEM and EDX; the relevant results are shown in Fig. 4 and Fig. 5. As shown in Fig. 4, the samples are composed of nanoflakes, which is consistent with the results shown in Fig. 1. In Fig. 4a, one can notice a black rod-like feature which may be an impurity introduced during the preparation of TEM samples. In addition, Fig. 4a and 4c show large clusters which may result from the aggregation of MoSe₂ nanoflakes.

Fig. 5. EDX spectra of samples A, B and C. all the spectra show the peaks related to Se and Mo elements, which indicate that the nanoflakes are composed of Se and Mo elements.

They do not affect our study on the structure and composition of MoSe_2 nanoflakes since we are interested in clear MoSe_2 nanoflakes located near the edge areas of clusters. The selected area electron diffraction (SAED) patterns shown in Fig. 4 indicate that the formed MoSe_2 nanoflakes have a crystalline structure. Figure 5 presents the EDX spectra of samples A, B and C obtained during TEM measurement. As can be seen in this figure, all spectra show the peaks related to Se and Mo elements, which indicate that the nanoflakes are composed of Se and Mo elements.

Additional characterization of the binding states of Se and Mo elements in samples A and C was done by XPS. The atomic concentrations of Mo, Se and O elements obtained from the XPS results are listed in Table 3 and shown in Fig. 6. According to these results, the ratio of Se to Mo atoms is about 1.5 and 1.7 for samples A and C, respectively.

Furthermore, the Mo 3d and Se 3d XPS spectra (see Fig. 6) were fitted using standard XPS fitting software after Shirley background subtraction. The positions of fitted peaks shown in Fig. 6 are listed in Table 4. Specifically, the $^1\text{Mo } 3d_{5/2}$ and $^1\text{Se } 3d_{5/2}$ peaks are same as the peaks of MoSe_2 reported elsewhere [18,19]; the $^2\text{Mo } 3d_{5/2}$ and the $^2\text{Mo } 3d_{3/2}$ peaks are attributed to MoO_2 [20], and the $^3\text{Mo } 3d_{5/2}$ peak is related to Mo^{+5} in molybdenum oxide, respectively [21,22].

Using Fig. 6, we have obtained the integrated areas of peaks, and the results indicate that the area ratio of $^1\text{Mo } 3d_{5/2}$ to $^1\text{Mo } 3d_{3/2}$ peaks approaches the area ratio of $^2\text{Mo } 3d_{5/2}$ to $^2\text{Mo } 3d_{3/2}$ peaks (the ratios are ~ 1.4 and 1.5).

Fig. 6. Mo 3d and Se 3d XPS spectra of samples A and C. The $^1\text{Mo } 3d_{5/2}$ and $\text{Se } 3d_{5/2}$ peaks are consistent with the XPS peaks of MoSe_2 and the $^2\text{Mo } 3d_{5/2}$ and $^2\text{Mo } 3d_{3/2}$ peaks are attributed to MoO_2 , respectively. The $^3\text{Mo } 3d_{5/2}$ peak is related to Mo^{+5} in molybdenum oxide.

In Fig. 6, the Mo 3d XPS spectra show the $^3\text{Mo } 3d_{5/2}$ peak of Mo^{+5} in molybdenum oxide, but the $^3\text{Mo } 3d_{3/2}$ peak is not clearly visible in the XPS spectra; it may be due to very weak $^3\text{Mo } 3d_{5/2}$ peak. The intensity of the $^3\text{Mo } 3d_{5/2}$ peak is close to the detection limit and is very low, so the $^3\text{Mo } 3d_{3/2}$ peak could not be resolved, possibly because its intensity fell below the instrument's detection threshold.

From Fig. 6 the integral intensity of the peaks related to Mo was also obtained which show that the amount of Mo^{+4} and Mo^{+5} related to molybdenum oxides is of about 54% for sample A, and it is of about 41 % for sample C. This is an apparent evidence of the effect of hydrogen reduction on the specific morphology of sample A as compared to sample C produced using nitrogen. This indicates that hydrogen has a stronger reduction capacity for MoO_3 than nitrogen.

Table 3. Atomic concentrations of Mo, Se and O elements

Sample	Se (atm.%)	Mo (atm.%)	O (atm.%)	Ratio of Se to Mo atoms
A	22.89	14.81	2.79	1.5
C	21.82	13.20	1.90	1.7

Table 4 Positions of fitted peaks in Fig.6

Sample	$^1\text{Mo } 3d_{3/2}(\text{eV})$	$^1\text{Mo } 3d_{5/2}(\text{eV})$	$^2\text{Mo } 3d_{3/2}(\text{eV})$	$^2\text{Mo } 3d_{5/2}(\text{eV})$	$^3\text{Mo } 3d_{5/2}(\text{eV})$	$^1\text{Se } 3d_{3/2}(\text{eV})$	$\text{Se } 3d_{5/2}(\text{eV})$
A	232.43	229.25	232.80	229.60	230.81	55.7	54.9
C	232.43	229.22	232.79	229.62	230.79	55.7	54.8

Figures S1 and S2 (Supporting Information) show the SEM images and Raman spectra of samples synthesized under different conditions. The Raman spectra shown in Fig. S2 evidence the formation of thick MoSe_2 nanoflakes, thus indicating the repeatability of the experiments. Comparison of SEM images of the samples grown under different conditions evidences that the increase of gas flow rate leads to the improvement of aggregation of MoSe_2 nanoflakes, while the high pressure weakens the aggregation.

3.2 Formation of MoSe_2 nanoflakes

To date, various modes of CVD growth of MoSe_2 nanoflakes have been extensively studied. For example, MoO_3 and Se powders were used as source materials to synthesize the MoSe_2 flakes in the process environments of pure hydrogen or argon gases or their mixtures [11-14]. However, the conclusions about the formation process of MoSe_2 nanoflakes remain somewhat conflicting. It was suggested that hydrogen plays an important role in the growth of MoSe_2 flakes [13,14], while Xia et al. believed that hydrogen cannot improve the growth of MoSe_2 [11]. Our results indicate that hydrogen can improve the growth of MoSe_2 . In this section, the formation and growth mechanisms of MoSe_2 nanoflakes are analyzed according to the possible reactions in different gas environments.

Hydrogen reacts with MoO_3 as follows [23]:

In early report [23], MoS_2 was synthesized in argon environment via the following possible reactions after evaporation of MoO_3 and S:

In our experiments, argon was replaced by hydrogen, nitrogen or a hydrogen-nitrogen gas mixture. Let us now examine the latter case of the hydrogen and nitrogen gas mixture. Due to the high temperature of filaments, H_2 easily decomposes into atomic hydrogen. Consequently, the following reactions can take place due to the evaporation of MoO_3 and Se,

It was reported that the intermediate product Mo_4O_{11} was formed at high temperature during the reduction of MoO_3 by hydrogen [24], thus indicating that MoO_{3-x} can be formed through reactions (4) and (5). Due to instability of MoO_{3-x} , it is further reduced by Se into MoSe_2 , since Mo_4O_{11} can be easily reduced by hydrogen into MoO_2 [24].

With hydrogen present in the reaction gas mixture, why does MoSe_2 turns out to be a final product? Apparently, this is related to the gas transport effects. During the substrate heating, Se powder gradually evaporates and this means that the silicon substrate is covered by hydrogen, i.e., MoO_3 is mainly reduced by hydrogen into MoO_{3-x} or MoO_2 according to reaction (1). When sufficient amount of Se powder is evaporated, diffusion rate of Se atoms becomes relatively low because of their large mass. As a result, Se atoms densely populate the silicon substrate, which increases collision rates of Se and H atoms and eventually hindering

the diffusion of hydrogen atoms on the silicon surface. In this case, MoO_{3-x} is reduced by Se into MoSe_2 . Simultaneously, the formed MoO_2 species can be reduced by Se to form MoSe_2 species [25]. MoO_2 is stable compared to MoO_{3-x} , thus MoO_2 is partially reduced by Se. As a result, some MoO_2 species remain in the samples as impurities, and this is confirmed by the Raman and XPS results.

Although N_2 is a stable molecule, the high ($\sim 1800^\circ\text{C}$) filament temperature leads to the decomposition of some of N_2 molecules, so MoO_3 is also reduced by nitrogen alongside with hydrogen, leading to the formation of MoO_2 phase. This explains the appearance of the peaks related to molybdenum oxide in the Raman and XPS spectra of sample C in Fig. 3 and 6.

The electronegativity values for H, Se and N elements are 2.1, 2.4 and 3.0, respectively [26]. In other words, the ability of losing electrons (and hence the reduction capacity) becomes weaker along the sequence of H, Se and N elements when they react with other elements. Thus, the reduction capacity of H is strongest compared to the two other elements. As a result, the strong reduction capacity of hydrogen leads to a high formation rate of MoO_{3-x} at the initial formation stage of MoSe_2 according to reactions (4) and (5), which can be confirmed by the areas marked by red rings shown in Fig.2. Due to the high formation rate of MoO_{3-x} , reaction (6) is accelerated, i.e., hydrogen can accelerate the formation of MoSe_2 species. MoSe_2 species in turn deposit on the substrate surface to form MoSe_2 nanoflakes [11], thus the growth rate of MoSe_2 nanoflakes is high in the hydrogen-containing environment. After the MoSe_2 nanoflakes form, MoSe_2 species deposited on the substrate surface diffuse toward the edges of MoSe_2 nanoflakes and bond to the edges, which results in the growth of MoSe_2 nanoflakes.

The intrinsic silicon oxide on the silicon surface is reduced by hydrogen during the

growth of MoSe₂ nanoflakes. Thus, the density of dangling bonds on the silicon surface increases, leading to more MoSe₂ nucleation centers, as evidenced by the higher density of nanoparticles (including some nanoflakes) in the MoSe₂-Si interface of sample A, as shown in Fig. 2. Consequently, the formation of MoSe₂ nanoflakes is further improved. Continuously deposited MoSe₂ species lead to the growth of multilayer MoSe₂ nanoflakes because the MoSe₂ nanoflakes are grown in a layer-by-layer mode confirmed by Figs. 1 and 2. When the reaction gases lack hydrogen, the rate of MoSe₂ species formation decreases. As a result, the formed MoSe₂ species easily connect with the edges of MoSe₂ nanoflakes due to the presence of defects at the edges [27, 28]; this is the reason of larger MoSe₂ nanoflakes near the MoSe₂-Si interface of sample C, as shown in Fig. 2.

Due to the presence of MoO₂ compound in MoSe₂ nanoflakes as impurity, an internal stresses is produced in the nanoflakes. When the internal stress is large enough, the MoSe₂ nanoflakes on the silicon surface switches to tilt growth (as the upward growth of graphene is caused by stress [29]), thus Figs.1 and 2 shows the MoSe₂ nanoflakes tilted with respect to the silicon substrate. In addition, the tilt growth of MoSe₂ is also related to some defects such as dislocations and local disordering besides of the effect of stress, which is evidenced by vertical growth of MoS₂ nanoflakes due to the coalescence of adjacent flakes [30].

The high reduction capacity of hydrogen leads to the deposition of more MoO_{3-x} species onto the surfaces of formed MoSe₂ nanoflakes, i.e., there are more defects on the surfaces. As a result, more MoSe₂ nanoflakes nucleate on the surfaces of the growing MoSe₂ nanoflakes, as confirmed by the areas marked with red rings in Fig. 2.

Figure 1 shows the rough surfaces of MoSe₂ nanoflakes of samples A and B, i.e., some islands form on surfaces of MoSe₂ nanoflakes. Simultaneously, the similar result was

observed on surfaces of MoSe₂ sheets grown from Ar + H₂ environment [13]. The formation of islands may be related to the formation rate of MoSe₂ species. During growth of MoSe₂ nanoflakes, reactions (5) and (6) can occur on the surfaces of formed MoSe₂ nanoflakes due to the deposition of MoO_{3-x} and Se species. From the above analyses it follows that the formation rate of MoO_{3-x} species in the environment containing hydrogen is high, which can result in the aggregation of MoO_{3-x} species deposited on the surfaces of formed MoSe₂ nanoflakes. Next, the aggregated MoO_{3-x} species react with Se species and form the aggregated MoSe₂ species (i.e., MoSe₂ islands) because it is difficult for them to diffuse on the surfaces of formed MoSe₂ nanoflakes due to their large mass. However, the formation rate of MoO_{3-x} species is low in nitrogen environment, so it is difficult for the MoO_{3-x} species to aggregate and thus the formed MoSe₂ species easily diffuse on the surfaces of formed MoSe₂ nanoflakes. Apparently, it is the possible reason that the surfaces of MoSe₂ nanoflakes in samples A and B are rough compared to that of sample C (see Fig. 1). Conversely, the formation of MoSe₂ islands on the surfaces of MoSe₂ nanoflakes suggests the high formation rate of MoSe₂ species in the gas environment containing hydrogen. In addition, we should note that the formation of MoSe₂ on the surfaces of islands simultaneously hinders the surface reactions of Se species with the MoO_{3-x} species, thus more MoO_{3-x} species remain in samples A and B. This is the reason why the XPS results show a higher content of molybdenum oxide in sample A than in sample C.

Comparison of the Raman results with the XPS results evidences that Raman spectrum of sample A shows well formed MoSe₂, while XPS results of sample A indicate that this sample contains more molybdenum oxide. Since hydrogen can improve the formation of MoSe₂ species, one naturally can ask why the Raman and XPS results of sample A exhibit

such a large difference? Apparently, it relates to the measurement depth of instruments and the amount of source materials. During the growth of samples, the amount of MoO₃ and Se powders is limited. As a result, Se fast spends in the initial growth of MoSe₂ in hydrogen environment due to the high formation rate of MoO_{3-x} species; thus, more MoO_{3-x} species remain on the MoSe₂ nanoflakes in the final growth of MoSe₂. It is known that the measurement thickness of XPS is lower than that of Raman spectroscopy, thus the molybdenum oxide component on the MoSe₂ nanoflakes can easily be detected by XPS. This is the reason why the Raman and XPS results of sample A present the large difference.

Regarding the conflicting results of the hydrogen effect on the growth of MoSe₂ flakes [11,13,14], the likely reasons for these discrepancies are related to the growth temperature and design of CVD equipment. In these examples, the MoSe₂ sheets were synthesized in thermal CVD process where the surface temperature of a silica tube is usually higher than the gas temperature (since heating is provided at the outer side of the tube). Due to the formation of MoSe₂ species mainly in the gas phase, the density of MoSe₂ species is rather low near the substrate surface. Consequently, the direction of the temperature gradient is opposite to the direction of the species concentration gradient, and hence temperature gradient reduces diffusion rate of MoSe₂ toward the substrate. From the reduction of MoO₃ by carbon it follows that the process of forming MoO₂ is exothermal [31], which implies that the formation of MoSe₂ may be an exothermal process. However, the deposition of MoSe₂ molecules on the substrate is also an exothermal process according to formula $\Delta G = \Delta H - T\Delta S$, where ΔG , ΔH and ΔS are the change of Gibbs free energy, heat and entropy, respectively. When MoSe₂ molecules deposit onto the substrate, their motion changes from three dimensions to two dimensions, which leads to $\Delta S < 0$. Due to the spontaneous

deposition of MoSe₂ molecules, ΔG is negative. Thus, $\Delta H < 0$, i.e., the deposition of MoSe₂ molecules on the substrate is an exothermal process. In other words, reaction heat also contributes to the MoSe₂ structure formation along with the heat supplied externally by the hot filaments.

In the above mentioned CVD processes, the growth temperatures were 820 °C [11] and 750 °C [13,14]. Such a temperature results in a high temperature gradient, so the diffusion rate of MoSe₂ species toward the substrate surface is low and most of the generated MoSe₂ species are driven to the end of the tube by the vacuum pump. As a result, the MoSe₂ nanosheets cannot be grown in the mixture of hydrogen and argon gases [11].

To summarize, hydrogen indeed can enhance the formation of MoO_{3-x} species and create more nucleation centers to promote the growth of MoSe₂ nanoflakes in HFCVD system.

3.3 PL properties of MoSe₂ nanoflakes

Fig. 7. PL spectra of samples A, B and C. The inset is narrow-scan of PL spectra of samples A and B in the 600-700 nm range.

Figure 7 shows the PL spectra of samples A, B and C, and the inset in Fig. 7 shows the narrow-scan of PL spectra of samples A and B in the 600-700 nm range. Figure S3(c) in the

Supporting Information shows the PL emission from a thick plane MoSe₂ nanoflake on silicon substrate. There is no notable PL band, apparently due to a very weak PL emission from thick, plane MoSe₂ nanoflakes. The thickness of monolayer MoSe₂ is about 0.71 nm [11], while the thickness of typical thin MoSe₂ nanoflakes in our samples was ~10 nm, i.e., the nanoflakes in our samples are thick MoSe₂. However, thick MoSe₂ emits very weak PL band at about 805 nm [11], and Fig. S3(c) does not show notable PL band. The XPS results indicate that the samples contain molybdenum oxide impurities, however MoO₂ emits the ultraviolet and blue light [32], and the PL band of MoO₃ locates at about 750 nm at 4.2 K [33]. Thus, the PL bands at about 631 nm shown in Fig.7 may be emitted by the edges of MoSe₂ nanoflakes. The origin of this major difference in the observed PL properties is possibly related to the PL emission zone difference between the samples.

Plane MoSe₂ nanoflake rested on silicon substrate generates PL emission from the surface, since the excitation laser light irradiates the surface of nanoflake during the PL measurements; thus, the PL properties of MoSe₂ nanoflake are determined by the thickness of the nanoflake. However, samples A-C are composed of MoSe₂ nanoflakes tilted with respect to the silicon substrate, i.e., most of the edges of MoSe₂ nanoflakes are irradiated by the excitation laser light during PL measurement and the PL properties should be determined by the edges of MoSe₂ nanoflakes.

The edges of MoSe₂ nanoflakes are terminated with the MoSe₂ species from diffusion of the formed MoSe₂ species in gas environment, thus the MoSe₂ clusters were formed on the edges of MoSe₂ nanoflakes. These MoSe₂ clusters can be composed of one or more MoSe₂ species, i.e., these MoSe₂ clusters are similar to quantum dots, which have wide bandgaps compared to MoSe₂ sheets (like Si quantum dots [34]). As a result, the blue shift PL bands related to MoSe₂ nanoflakes can be generated from the edges of MoSe₂ nanoflakes, while the

porous silicon materials can generate the great blue shift PL bands compared to bulk silicon [35, 36]. It is the possible reason that samples A-C emit the PL bands at about 631 nm, which have a great blue shift relative to the PL band of thick plane MoSe₂ nanoflake.

Fig. 7 shows that sample C generates stronger PL band than samples A and B, which is related to the amount of molybdenum oxide in the samples. In section 3.1 the XPS results were analyzed and it was indicated that the amount of Mo⁴⁺ and Mo⁵⁺ in molybdenum oxide is about 54% and 41% for samples A and C, respectively; these data imply that samples A and B contain more molybdenum oxide than sample C, thus indicating relatively reduced amount of MoSe₂ in samples A and B. As a consequence, the number of emissive centers in samples A and B is reduced, so their PL intensity is weakened. According to the analyses shown in section 3.2, the residual molybdenum oxide mainly results from the aggregation of MoO_{3-x} species on the surfaces of MoSe₂ nanoflakes due to strong reduction of hydrogen [37, 38], thus the PL properties of MoSe₂ nanomaterials grown in the gas environment containing hydrogen are weakened.

4. Conclusion

In summary, MoSe₂ nanoflakes have been synthesized by HFCVD in different gas environments. Structural and PL properties of the synthesized MoSe₂ nanoflakes were studied using FESEM, TEM, XPS and micro-Raman spectroscopy, respectively. According to the characterization results, the effect of hydrogen on the structure and PL properties of MoSe₂ nanoflakes was studied. The important role of hydrogen at the initial growth of MoSe₂ nanoflakes and deterioration of PL properties was confirmed. The XPS results show a strong hydrogen reduction capacity towards MoO₃, which leads to a high formation rate of MoSe₂ at

the initial growth of MoSe₂ nanoflakes. However, strong reduction capacity of hydrogen simultaneously results in the increase of the amount of molybdenum oxide components in MoSe₂ samples, so the MoSe₂ samples generate a weak photoluminescence. These results can be used to control the growth process, morphology and microstructure of the MoSe₂-based and many other nanomaterials [39], which is relevant to the development of next-generation TMD-based optoelectronic functionalities and devices

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Effects of hydrogen on the structural and optical properties of MoSe₂ grown by hot filament chemical vapour deposition

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Highlights

- Plasma-enhanced chemical synthesis of molybdenum selenide nanoflake is demonstrated
- Inexpensive precursors in the low-temperature reactive plasma environment were used
- Self-organized growth mechanism of molybdenum selenide nanoflakes is proposed